Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary Information

Efficient Reverse Intersystem Crossing Process Exploiting Non-Bonding States in Inverted Singlet-Triplet Gap System

Hwon Kim[a], Seung Kyu Min[a]

a. Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), South Korea

Optimized Geometries of Molecules

All the coordinates are in Angstroms.

Molecule 1

S_0 Geometry

C	1.40070400	-0.14704500	-0.00012200
C	1.53794600	2.11728300	-0.00007800
C	-0.57302700	1.28653800	0.00008000
N	0.00001600	-0.00003200	0.00000000
C	-2.60265000	0.27318000	0.00022600
C	-0.82759700	-1.13966800	0.00004200
C	1.06469000	-2.39052300	-0.00014800
N	1.92741800	-1.37465800	-0.00019600
N	-1.90318100	1.40788300	0.00019500
N	0.22679900	2.35645300	0.00003900
N	2.17087500	0.94424200	-0.00016000
N	-2.15428600	-0.98181000	0.00015800
N	-0.26769300	-2.35188800	-0.00003500
H	-3.68503300	0.38701500	0.00032100
H	1.50741600	-3.38475500	-0.00021000
H	2.17759500	2.99782400	-0.00011100

S_1 Geometry

C	1.36919100	-0.34168600	0.03656200
C	0.72593900	-2.53364300	-0.00914500
C	-0.98054200	-1.01492000	0.03626900
N	-0.00003300	-0.00000700	0.26676300
C	-2.55715800	0.63819100	-0.00939100
C	-0.38867500	1.35656800	0.03618100
C	1.83123600	1.89551100	-0.00921300
N	2.27539700	0.62618100	-0.05470600
N	-2.26177800	-0.67377000	-0.05519400
N	-0.59541200	-2.28364700	-0.05507100
N	1.71441100	-1.62183600	-0.05467800
N	-1.67994600	1.65744400	-0.05523900
N	0.54736200	2.29560400	-0.05520300
H	-3.60970100	0.90086700	-0.01485900
H	2.58497700	2.67572000	-0.01475200
H	1.02476700	-3.57649600	-0.01467700

T(π-π*) Geometry

C	-1.14643900	0.83264300	0.01813100
C	0.27516900	2.62265700	-0.00830300
C	1.29428800	0.57653500	0.01810100
N	0.00000800	-0.00001900	0.12237300
C	2.13369400	-1.54960800	-0.00775600
C	-0.14786100	-1.40909200	0.01828900
C	-2.40892700	-1.07299400	-0.00783100
N	-2.35094600	0.27373800	-0.02353100
N	2.35656700	-0.22018500	-0.02357800
N	1.41261300	1.89903600	-0.02402900
N	-0.98762900	2.15091400	-0.02372100
N	0.93836400	-2.17285100	-0.02338700
N	-1.36890700	-1.93075100	-0.02332800
H	3.01112500	-2.18686000	-0.01603300
H	-3.39949200	-1.51427600	-0.01609900
H	0.38831600	3.70111300	-0.01724000

Molecule 2

S_0 Geometry

C	0.29923800	-1.24761000	0.00001000
C	-1.68108500	-0.13484100	0.00004900
C	0.17803200	1.18625900	-0.00001900
N	0.94263400	0.00703400	-0.00003100
C	2.13051200	2.33852600	-0.00011300
H	2.62370900	3.30862600	-0.00015100
C	2.34839700	0.07979100	-0.00007800
C	2.36462900	-2.18814300	-0.00002400
H	2.95736900	-3.10078400	-0.00001600
N	1.04345400	-2.35741800	0.00002100
N	0.79607000	2.36893100	-0.00006300
N	-1.15490200	1.09349900	0.00003800
N	-1.03256800	-1.29976200	0.00003600
C	-3.21589800	-0.21004100	0.00006200
O	-3.75610900	-1.29410500	-0.00022000
C	-3.96603600	1.10053900	0.00041400
H	-5.03742900	0.89341400	0.00045200
H	-3.69548100	1.70017400	0.87639200
H	-3.69561800	1.70055500	-0.87534500
N	2.93841500	1.27998700	-0.00012100
N	3.05969300	-1.04884600	-0.00007700

S_1 Geometry

C	0.27731700	-1.24019000	0.08543900
C	-1.71733400	-0.11190500	0.07883800
C	0.16911800	1.19331800	0.05283500
N	0.93300200	0.00790200	-0.11598600
C	2.13738800	2.34675100	-0.04194500
H	2.64303600	3.30783600	-0.06483800
C	2.34136300	0.07496900	-0.10082400
C	2.34909700	-2.20658800	-0.00278300
H	2.93980700	-3.11823300	-0.01577600
N	1.03606100	-2.35511900	0.14582000
N	0.81441500	2.37599100	0.07928200
N	-1.13466300	1.11007600	0.17050300
N	-1.02638900	-1.29213100	0.16993300
C	-3.18329500	-0.20205200	-0.06284600
O	-3.70835700	-1.29763300	-0.24417500
C	-3.98470900	1.08151900	-0.00075600
H	-5.03412300	0.85475000	-0.19650500
H	-3.88456100	1.55116900	0.98457100
H	-3.61181300	1.80465900	-0.73461700
N	2.94095300	1.25931900	-0.09512500
N	3.04817000	-1.05376100	-0.07830900

T(π-π^*) Geometry

C	0.28235700	-1.24931800	-0.00007500
C	-1.73033200	-0.12860000	0.00007900
C	0.16121900	1.19049100	-0.00001400
N	0.95703900	0.00746600	-0.00019500
C	2.13413600	2.35398800	-0.00005800
H	2.64022700	3.31550600	-0.00005700
C	2.33724200	0.07986100	-0.00014300
C	2.36751700	-2.20504800	-0.00015100
H	2.96707700	-3.11138500	-0.00018300
N	1.05305500	-2.36762300	-0.00008500
N	0.81255200	2.38081400	0.00002600
N	-1.13978100	1.10779100	0.00006900
N	-1.01688700	-1.30883000	0.00004700
C	-3.20529700	-0.20999700	0.00018500
O	-3.76961400	-1.29738000	0.00021700
C	-3.97157400	1.10098500	0.00025300
H	-5.03954400	0.87558000	0.00033400
H	-3.71967200	1.70642100	0.87824800
H	-3.71981000	1.70643900	-0.87776900
N	2.94972200	1.26676700	-0.00010300
N	3.06673300	-1.04462900	-0.00015500

T(n-π*) Geometry

C	0.25778600	-1.23437000	0.00000500
C	-1.70157400	-0.04950600	0.00000400
C	0.19710500	1.21882700	0.00000200
N	0.93820300	0.01115200	0.00000100
C	2.18645400	2.31116400	-0.00000400
H	2.70831600	3.26653400	-0.00000600
C	2.34342300	0.04703800	-0.00000300
C	2.30325600	-2.22094900	0.00000200
H	2.87546600	-3.14707600	0.00000200
N	0.98175200	-2.36364300	0.00000700
N	0.85659300	2.38369200	-0.00000100
N	-1.12349700	1.16340700	0.00001000
N	-1.06231100	-1.25668700	0.00000400
C	-3.12271500	-0.14205200	-0.00000300
O	-3.66785500	-1.30798400	-0.00001700
C	-4.05194600	1.04532300	0.00000500
H	-4.69348100	1.03235200	0.88789800
H	-3.42368500	1.94058700	-0.00000100
H	-4.69349700	1.03235200	-0.88787700
N	2.96703800	1.22963600	-0.00000600
N	3.02779300	-1.09808900	-0.00000300

Molecule 3

S_0 Geometry

C	1.00656600	-1.26851500	-0.00022100
C	-1.05639700	-0.32594400	-0.00007700
C	0.68058300	1.14988100	-0.00020200
N	1.53928200	0.03730800	-0.00028800
C	2.52885700	2.46160600	-0.00041700
H	2.93767500	3.46992700	-0.00046900
C	2.93368300	0.22858400	-0.00042500
C	3.14379100	-2.02990300	-0.00037000
H	3.81041900	-2.88976600	-0.00038600
N	1.83938600	-2.30939500	-0.00025400
N	1.19478500	2.37826800	-0.00027700
N	-0.64165200	0.94316800	-0.00005300
N	-0.31905300	-1.43285200	-0.00012900
C	-2.57435800	-0.52816200	0.00013100
O	-3.05226200	-1.63479400	0.00010500
N	3.42035500	1.47441100	-0.00047800
N	3.73762100	-0.83653100	-0.00046000
C	-3.40674500	0.75966800	0.00065500
H	-3.12955700	1.36857400	0.87009900
H	-3.13020600	1.36880600	-0.86883300
C	-4.84445000	0.50133600	0.00115700
N	-5.99064100	0.32698100	0.00156200

S$_1$ Geometry

C	0.98351800	-1.26744400	-0.00004600
C	-1.09939200	-0.32258200	0.00024700
C	0.66417700	1.14580200	0.00003200
N	1.54185700	0.03761700	-0.00076300
C	2.52695500	2.47794000	-0.00045700
H	2.95121400	3.47769000	-0.00049700
C	2.93696900	0.22746500	-0.00079700
C	3.14055300	-2.05177300	-0.00059700
H	3.81577700	-2.90253200	-0.00076500
N	1.84679800	-2.32115900	0.00002600
N	1.20759600	2.39148400	0.00013800
N	-0.62685800	0.96092200	0.00056600
N	-0.30426000	-1.43935100	0.00040500
C	-2.56127300	-0.52178400	-0.00007400
O	-3.06090400	-1.63563200	0.00041300
N	3.43006200	1.45965700	-0.00074000
N	3.74120300	-0.83074200	-0.00083300
C	-3.40506200	0.76799000	0.00041700
H	-3.14764300	1.38178300	0.87236000
H	-3.14818700	1.38195900	-0.87155800
C	-4.84101900	0.49450700	0.00084600
N	-5.98732300	0.31949200	0.00116200

T(π-π*) Geometry

C	0.98555600	-1.26940900	0.03719600
C	-1.10811200	-0.31737200	0.03571900
C	0.66573900	1.15254700	0.01976000
N	1.55099500	0.03863700	-0.00998800
C	2.53498200	2.47306200	-0.02622800
H	2.96007600	3.47306400	-0.03757800
C	2.92156500	0.22382100	-0.03522100
C	3.14125000	-2.04994900	-0.00507500
H	3.81307500	-2.90411800	-0.01132100
N	1.84518700	-2.32006300	0.04700400
N	1.21529300	2.39247600	0.01302200
N	-0.62411000	0.96397000	0.06081000
N	-0.30463900	-1.43791700	0.05505100
C	-2.55928400	-0.51995700	-0.00388500
O	-3.05958900	-1.63052700	-0.09776500
N	3.43360400	1.45760600	-0.04955800
N	3.74011000	-0.83738700	-0.03873100
C	-3.41145000	0.76380100	0.06791600
H	-3.18775600	1.30550400	0.99532500
H	-3.12009800	1.44323600	-0.74254600
C	-4.84533300	0.49244100	-0.00794600
N	-5.99045100	0.31876600	-0.06549200

T(n-π*) Geometry

C	0.95528000	-1.28130200	0.01560400
C	-1.12257100	-0.39817200	-0.28917500
C	0.56510000	1.13443400	-0.18729200
N	1.45468200	0.04722700	-0.00590700
C	2.37345200	2.49875100	-0.05860600
H	2.75758200	3.51688100	-0.08042500
C	2.83133900	0.28536100	0.14656200
C	3.10099600	-1.96013100	0.32118300
H	3.78877100	-2.79254400	0.45804400
N	1.81965600	-2.29047900	0.18354700
N	1.05542000	2.37841700	-0.21406900
N	-0.72749200	0.89176500	-0.32615500
N	-0.34129700	-1.49828000	-0.12941200
C	-2.51540900	-0.64721900	-0.44271200
O	-3.01522000	-1.82118400	-0.44985000
N	3.28542200	1.54253200	0.11954300
N	3.65983400	-0.74712900	0.31414400
C	-3.52666600	0.48684200	-0.63577900
H	-2.90696000	1.38572600	-0.74573300
H	-4.09972900	0.32018500	-1.55553300
C	-4.44127200	0.63573800	0.49616300
N	-5.16899600	0.76357900	1.39070600

Molecule 4

S_0 Geometry

C	0.74896300	-1.26310800	0.00673400
C	-1.29264900	-0.26905000	-0.02383000
C	0.48417000	1.15998900	-0.02060500
N	1.31684200	0.02725600	0.00037700
C	2.36586400	2.42479700	-0.01904800
H	2.80110700	3.42216700	-0.02838800
C	2.71554900	0.18301500	0.01417800
C	2.86580100	-2.08000100	0.04338500
H	3.51042500	-2.95652200	0.06255200
N	1.55612900	-2.32669900	0.02959200
N	1.03209200	2.37668100	-0.03217500
N	-0.84015000	0.98862800	-0.02760000
N	-0.57822200	-1.39372800	-0.01081600
C	-2.81412500	-0.43365000	-0.04480300
O	-3.30354500	-1.53918500	-0.13557200
N	3.23397500	1.41545000	0.00436000
N	3.49189400	-0.90255400	0.03623100
C	-3.65005100	0.82930400	0.00164400
H	-3.25123200	1.49301000	0.77944500
H	-3.44607800	1.35852700	-0.95075100
N	-5.04058200	0.50341700	0.25511200
H	-5.65205300	1.23564800	-0.09316600
H	-5.27877900	-0.36628300	-0.21661600

S_1 Geometry

C	-0.73666500	-1.26127600	0.04046100
C	1.32530500	-0.26847600	0.08509200
C	-0.47336400	1.15448900	0.04455200
N	-1.30841400	0.02579800	-0.17900900
C	-2.36350300	2.44001000	-0.02518000
H	-2.80672300	3.43113500	-0.04268700
C	-2.71407200	0.18280500	-0.09878400
C	-2.86849700	-2.09699900	-0.02248100
H	-3.51851500	-2.96684600	-0.03702500
N	-1.56657200	-2.32774800	0.09989000
N	-1.04285000	2.37749400	0.09841100
N	0.82182300	0.99504100	0.15941100
N	0.55682900	-1.39357400	0.15930100
C	2.79822500	-0.42687000	-0.00214900
O	3.30154500	-1.53860100	-0.10592000
N	-3.23480300	1.40237100	-0.05911100
N	-3.49137700	-0.89519700	-0.06106100
C	3.65885900	0.84301700	0.03893200
H	3.32220400	1.54014800	-0.73803600
H	3.47074900	1.36444900	0.98708600
N	5.08575900	0.59954400	-0.10856300
H	5.25405300	0.16574100	-1.01588000
H	5.36536300	-0.11210800	0.56637500

T(π-π*) Geometry

C	0.73595500	-1.26804400	-0.00002100
C	-1.33971800	-0.27003700	-0.00008200
C	0.46919700	1.16064000	-0.00003700
N	1.33370000	0.02730400	-0.00000600
C	2.36892800	2.44036200	0.00001100
H	2.81662700	3.43041700	0.00002500
C	2.70713100	0.18201800	0.00003200
C	2.87481300	-2.09700700	0.00004500
H	3.52800900	-2.96547700	0.00006500
N	1.57272200	-2.33805700	0.00000500
N	1.04797500	2.38806900	-0.00002600
N	-0.82438500	1.00060700	-0.00007500
N	-0.55758100	-1.40546600	-0.00005800
C	-2.80505600	-0.42895700	-0.00012400
O	-3.32275600	-1.54051900	0.00000300
N	3.24753300	1.40387700	0.00004300
N	3.50292400	-0.89629700	0.00005800
C	-3.66199000	0.84700900	-0.00001700
H	-3.39279600	1.45963400	0.87016700
H	-3.39300600	1.45960800	-0.87028700
N	-5.09768600	0.60644700	0.00015700
H	-5.32429900	0.01942200	0.80310600
H	-5.32446100	0.01925700	-0.80262600

T(n-π*) Geometry

C	0.72052700	-1.33097000	-0.02376000
C	-1.40537800	-0.51278900	0.07636400
C	0.25965100	1.07262400	0.08646100
N	1.19076000	0.01285200	0.02374900
C	2.03135900	2.49077400	0.07382900
H	2.38346500	3.52100700	0.09172200
C	2.56947800	0.28680200	-0.00819400
C	2.90694800	-1.95370000	-0.10681900
H	3.62816900	-2.76778500	-0.15776500
N	1.63194100	-2.31788700	-0.08888700
N	0.70831800	2.33690800	0.10355500
N	-1.02981200	0.79676300	0.12679900
N	-0.57111600	-1.58354300	-0.00677500
C	-2.81009100	-0.79153500	0.10371800
O	-3.38557300	-1.87763500	0.04192400
N	2.98416500	1.55929800	0.02353100
N	3.43558600	-0.72251600	-0.07137500
C	-3.82042000	0.49633200	0.33159800
H	-4.82975200	0.09879700	0.24414700
H	-3.59723500	0.79504900	1.36084600
N	-3.58362600	1.55309700	-0.55201500
H	-3.94356600	1.45847000	-1.49623100
H	-2.63245200	1.92550200	-0.48736600

EOM-CCSD energies of Each Excited States at Geometries Obtained at TDDFT, TDA, and UDFT

All the energies are in atomic units. The UDFT method cannot be applied to the singlet excited states and are thus listed as Not Applicable (N/A). N/A for other combinations of excited state and method indicates that the level of theory failed to converge into the relaxed geometry of the state. The geometries used for rate calculations are written in bold.

Table S1. Computed EOM-CCSD excited state energies of molecule 1 for each level of theory

	TDDFT	TDA	UDFT
S_1	**-611.9160**	-611.9159	N/A
T_1	N/A	**-611.9089**	N/A

Table S2. Computed EOM-CCSD excited state energies of molecule 2 for each level of theory

	TDDFT	TDA	UDFT
S_1	**-764.1532**	-764.1416	N/A
T(π-π*)	-764.1514	-764.1515	**-764.1521**
T(n-π*)	-764.1528	-764.1527	**-764.1531**

Table S3. Computed EOM-CCSD excited state energies of molecule 3 for each level of theory

	TDDFT	TDA	UDFT
S_1	**-856.1485**	N/A	N/A
T(π-π*)	-856.1484	-856.1486	**-856.1489**
T(n-π*)	**-856.1431**	-856.1407	N/A

Table S4. Computed EOM-CCSD excited state energies of molecule 4 for each level of theory

	TDDFT	TDA	UDFT
S_1	-819.3558	**-819.3561**	N/A
T(π-π*)	-819.3540	-819.3541	**-819.3547**
T(n-π*)	-819.3505	-819.3608	**-819.3639**

Computational Details: Intersystem Crossing

The Golden Rule rates of ISC/rISC between the S_1 state and the triplet states were calculated with the time-dependent correlation function formalism[1,2,3,4]. The Golden Rule rate in Fourier representation is as shown below:

$$k_{ISC/rISC} = \frac{|H_{SO}|^2}{\hbar}\int_{-\infty}^{\infty} d\tau \frac{1}{Z_i}\exp\left(-i\Delta E_{fi}^{ad}\tau\right)\cdot Tr[\exp\left(-i\hat{H}_{HO}\tau\right)\exp\left(-i\hat{H}'_{HO}\tau'\right)] \tag{1}$$

where ΔE_{fi}^{ad} is the adiabatic energy gap between the final and initial state, Z_i is the partition function of the vibrational states of initial state at temperature T, $\tau = t/\hbar$ and $'\tau = -\tau - i/k_BT$. The Hamiltonian $\hat{H}_{HO}$ is the harmonic oscillator Hamiltonian in the final state and the Hamiltonian $\hat{H}'_{HO}$ is the harmonic oscillator Hamiltonian in the initial state. The correlation function $Tr[\exp(-i\hat{H}_{HO}\tau)\exp(-i\hat{H}'_{HO}\tau')]$ can be expressed using the normal mode frequencies of the final state and the initial state, the Duschinsky rotation matrix between the final and initial state **S**, and the displacement vector **d**. From here on, the angular frequency of the μ-th mode of the final state will be denoted as ω_μ and that of the initial state will be denoted as ω'_μ. The Duschinsky rotation matrix and the displacement vector describes the relationship of normal mode coordinates of the final state **Q** and the normal mode coordinates of the initial state **Q'**:

$$\boldsymbol{Q}' = \boldsymbol{S}\boldsymbol{Q} + \boldsymbol{d} \tag{2}$$

In our calculation, the normal modes and frequencies for each state are obtained from the level of theory that gives the lowest energy in EOM-CCSD.

The frequencies form intermediate vectors as follows:

$$a_\mu = \frac{\omega_\mu}{\sin\left(\hbar\omega_\mu\tau\right)} \tag{3}$$

$$b_\mu = \frac{\omega_\mu}{\tan\left(\hbar\omega_\mu\tau\right)} \tag{4}$$

$$a'_\mu = \frac{\omega'_\mu}{\sin\left(\hbar\omega'_\mu\tau'\right)} \tag{5}$$

$$b'_\mu = \frac{\omega'_\mu}{\tan\left(\hbar\omega'_\mu\tau'\right)} \tag{6}$$

The intermediate vectors **a**, **a'**, **b**, and **b'**, the Duschinsky matrix, and the displacement vector form intermediate matrices and vectors as follows:

$$\boldsymbol{E} = diag(\boldsymbol{b}' - \boldsymbol{a}') \tag{7}$$

$$\boldsymbol{A} = diag(\boldsymbol{a}) + \boldsymbol{S}^T diag(\boldsymbol{a}')\boldsymbol{S} \tag{8}$$

$$\boldsymbol{B} = diag(\boldsymbol{b}) + \boldsymbol{S}^T diag(\boldsymbol{b}')\boldsymbol{S} \tag{9}$$

$$\boldsymbol{K} = \begin{bmatrix} \boldsymbol{B} & -\boldsymbol{A} \\ -\boldsymbol{A} & \boldsymbol{B} \end{bmatrix} \tag{10}$$

$$\boldsymbol{f} = |\boldsymbol{d}^T\boldsymbol{ES} \quad \boldsymbol{d}^T\boldsymbol{ES}|^T \tag{11}$$

The correlation function can be expressed using the intermediate matrices and vectors above as follows:

$$Tr\big[\exp\big(-i\hat{H}_{HO}\tau\big)\exp\big(-i\hat{H}'_{HO}\tau'\big)\big] = \sqrt{\frac{prod(\boldsymbol{a})prod(\boldsymbol{a}')}{\det(\boldsymbol{K})}} \times exp\left(-\frac{i}{\hbar}\left[\frac{1}{2}\boldsymbol{f}^T\boldsymbol{K}^{-1}\boldsymbol{f} - \boldsymbol{d}^T\boldsymbol{Ed}\right]\right) \tag{12}$$

Equation (13) will be inserted into Equation (2) to compute the k_{rISC}. The integration limit used in the work was [-2.42,2.42] ps with time step of 2.42 attoseconds for the ISCs/rISCs involving the T(π-π*) state and [-242,242] fs with time step of 0.242 attoseconds for the ISCs/rISCs involving the T(n-π*) state, corresponding to 10^6 points in the positive time direction. Shorter integration time and smaller time step was used for the T(n-π*) transitions due to the fast decay of integrands, which will be shown in Figure S3 and Figure S4 later on. For **1**, exponential damping in the form of $|e^{-\gamma\tau}|$ with $\tau = 5.0$ cm^{-1} was used for convergence of the integral.

Computational Details: Internal Conversion

The Golden Rule rate of IC between the two triplet states were calculated with the formalism of Miyazaki et al.[5] The rate was calculated with the integral below:

$$k_{IC} = \frac{1}{\hbar}\int_{-\infty}^{\infty} d\tau \frac{1}{Z_i}\exp\big(-i\Delta E_{fi}^{ad}\tau\big) \cdot \sum_{k,l}^{N} \boldsymbol{R_{kl}}\, \rho_{kl}(\beta,\tau) \tag{13}$$

With ΔE_{fi}^{ad}, Z_i, and τ defined as in the ISC/rISC calculation in Equation (1). The non-adiabatic coupling matrix elements $\boldsymbol{R_{kl}}$ are defined as

$$\boldsymbol{R}_{kl} = \left\langle \Phi_f \middle| -i\hbar\frac{\partial}{\partial Q_k} \middle| \Phi_i \right\rangle \times \left\langle \Phi_i \middle| -i\hbar\frac{\partial}{\partial Q_l} \middle| \Phi_f \right\rangle \tag{14}$$

Where Φ_f is the final electronic state, Φ_i is the initial electronic state, and $Q_{k,l}$ is normal coordinates of the k-th/l-th normal mode of the final electronic state. In our calculation, the normal modes and frequencies for each state are obtained from the level of theory that gives the lowest energy in EOM-CCSD.

The vibrational correlation function $\rho_{kl}(\beta,\tau)$ is

$$\rho_{kl}(\beta,\tau) = Tr\left[\left\{-i\hbar\frac{\partial}{\partial Q_k}\right\} exp\big(i\hat{H}_{HO}^{i}(\tau + i\beta)\big)\left\{-i\hbar\frac{\partial}{\partial Q_l}\right\} exp\big(-i\hat{H}_{HO}^{f}\tau\big)\right] \tag{15}$$

Which, in the singularity formalism, is computed as

$$\rho_{kl}(\beta,\tau) = \left(-\frac{1}{\sqrt{2}}\right)^N \left[\frac{\det(\boldsymbol{\Xi})}{\det(\boldsymbol{S}^T\boldsymbol{S})}\right]^{\frac{1}{2}} exp\left[-\frac{1}{\hbar}\boldsymbol{\zeta}^T\boldsymbol{\Psi}\right] \times \left[\frac{\hbar}{2}(\boldsymbol{S}^T\boldsymbol{\Omega}_i\boldsymbol{\Lambda})_{lk} + \big(\boldsymbol{\Omega}_f\boldsymbol{C}_{-}\boldsymbol{\eta}\big)_k(\boldsymbol{S}^T\boldsymbol{\Omega}_i\boldsymbol{A}\boldsymbol{\Psi})_l\right] \tag{16}$$

The correlation function contains diagonal matrices $\boldsymbol{\Omega}_{i,f}$, with each diagonal element

$$[\boldsymbol{\Omega}_i]_{kk} = \omega'_k, \qquad [\boldsymbol{\Omega}_f]_{kk} = \omega_k \tag{17}$$

The other matrices used in Equation (16) are defined as follows:

$$\mathbf{A}_{\pm,kk} = \left\{\left(e^{\beta\hbar\omega'_k} - 1\right)^{-1} + 1\right\} \pm \left(e^{\beta\hbar\omega'_k} - 1\right)^{-1} e^{i\hbar\omega'_k\tau} \tag{18}$$

$$\mathbf{C}_{\pm,kk} = 1 \pm e^{-i\hbar\omega_k\tau} \tag{19}$$

$$\boldsymbol{J} = \mathbf{A}_+\boldsymbol{\Omega}_i^{-1}(\boldsymbol{S}^T)^{-1}\boldsymbol{\Omega}_f\boldsymbol{C}_- + \mathbf{A}_-\boldsymbol{S}\mathbf{C}_+ \tag{20}$$

$$\boldsymbol{L} = \mathbf{C}_+\boldsymbol{S}^{-1}\mathbf{A}_- + \boldsymbol{C}_-\boldsymbol{\Omega}_f^{-1}\boldsymbol{S}^T\boldsymbol{\Omega}_i\mathbf{A}_+ \tag{21}$$

$$\boldsymbol{L}' = \mathbf{C}_-\boldsymbol{S}^{-1}\mathbf{A}_+ + \boldsymbol{C}_+\boldsymbol{\Omega}_f^{-1}\boldsymbol{S}^T\boldsymbol{\Omega}_i\mathbf{A}_- \tag{22}$$

$$\boldsymbol{\Xi} = (\mathbf{A}_+ + \mathbf{A}_-)(\mathbf{A}_+ - \mathbf{A}_-)(\boldsymbol{C}_+ - \mathbf{C}_-) \tag{23}$$

$$\boldsymbol{\Lambda} = \mathbf{A}_+\boldsymbol{L}^{-1}\boldsymbol{C}_+ - \mathbf{A}_-\boldsymbol{L}'^{-1}\mathbf{C}_- \tag{24}$$

$$\boldsymbol{\zeta} = \frac{\mathbf{A}_-}{\mathbf{A}_+}\boldsymbol{\Omega}_i\boldsymbol{d} \tag{25}$$

$$\boldsymbol{\eta} = \boldsymbol{J}^{-1}\mathbf{A}_-\boldsymbol{d} \tag{26}$$

$$\boldsymbol{\Psi} = \boldsymbol{d} - \boldsymbol{S}\boldsymbol{C}_+\boldsymbol{\eta} \tag{27}$$

The integration limit used in the work was [-48.4,48.4] fs with time step of 0.242 attoseconds for compound **2** and **3** and [-24.2,24.2] fs with timestep of 0.242 attoseconds for compound **4** due to the rapid decay of correlation function in the case of compound **4**.

For all rate calculations, the temperature was set to 300 K. The normal mode frequencies, Duschinsky matrix, and the displacement vectors were calculated using B3LYP functional with 6-31G(d) basis set using Gaussian software.[6] The rate calculations were performed with our own Fortran code.

Energies of Each Molecules in Each Geometries

All the energies are in eV, measured relative to the S_0 state's relaxed geometry energy.

Table S5. Computed energies of molecule 1 at each geometry

	S_0 Energy	S_1 Energy	T(π-π*) Energy
S_0 Geometry	0.000	2.792	2.969
S_1 Geometry	0.346	2.708	2.911
T(π-π*) Geometry	0.128	2.717	2.900

Table S6. Computed energies of molecule 2 at each geometry

	S_0 Energy	S_1 Energy	T(π-π*) Energy	T(n-π*) Energy	S(n-π*) Energy
S_0 Geometry	0.000	2.698	2.833	3.051	3.470
S_1 Geometry	0.334	2.683	2.758	3.067	3.471
T(π-π*) Geometry	0.310	2.708	2.713	3.027	3.435
T(n-π*) Geometry	0.541	3.072	3.121	2.688	3.107

Table S7. Computed energies of molecule 3 at each geometry

	S_0 Energy	S_1 Energy	T(π-π*) Energy	T(n-π*) Energy	S(n-π*) Energy
S_0 Geometry	0.000	2.687	2.801	3.201	3.619
S_1 Geometry	0.297	2.662	2.665	3.185	3.578
T(π-π*) Geometry	0.345	2.687	2.652	3.184	3.569
T(n-π*) Geometry	0.534	3.030	3.036	2.809	3.248

Table S8. Computed energies of molecule 4 at each geometry

	S_0 Energy	S_1 Energy	T(π-π*) Energy	T(n-π*) Energy	S(n-π*) Energy
S_0 Geometry	0.000	2.692	2.822	3.156	3.560
S_1 Geometry	0.291	2.560	2.654	3.055	3.445
T(π-π*) Geometry	0.221	2.604	2.601	2.934	3.321
T(n-π*) Geometry	0.750	3.286	3.334	2.347	2.639

Orbital Configuration of Excited States

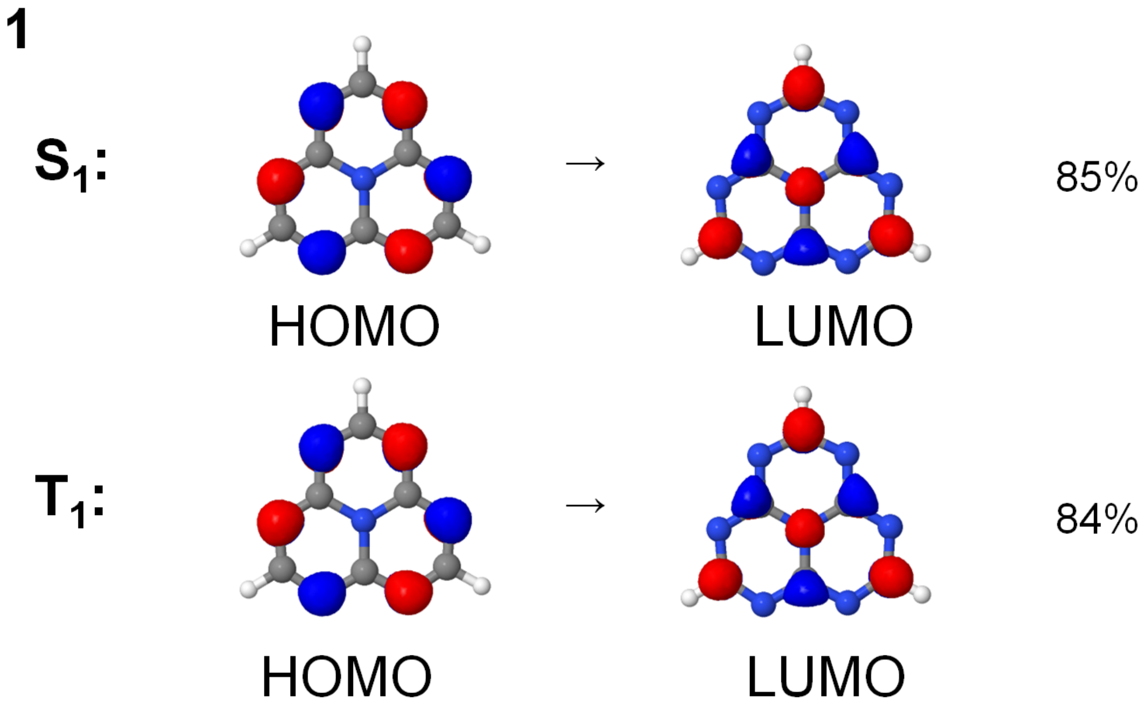

Figure S1. Dominant transitions of Molecule **1** for S_1 and T_1 state at S_0 geometry

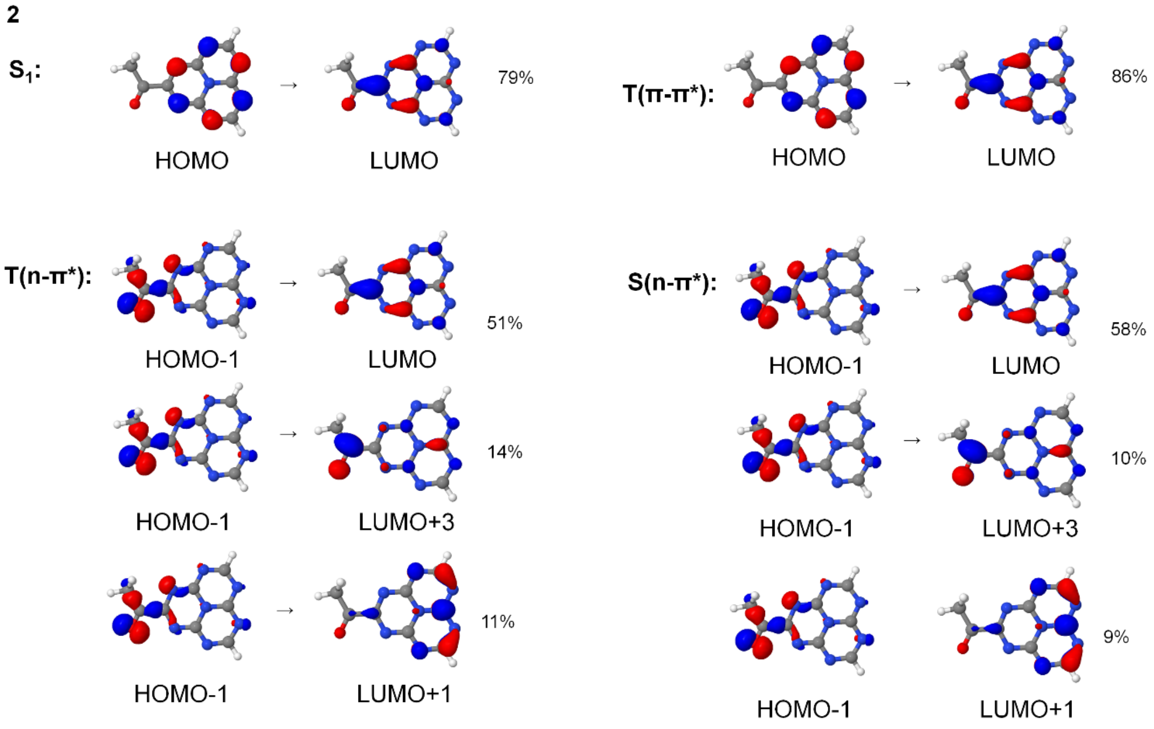

Figure S2. Dominant transitions of Molecule **2** for S_1, T(π-π*), and T(n-π*) state at S_0 geometry

3

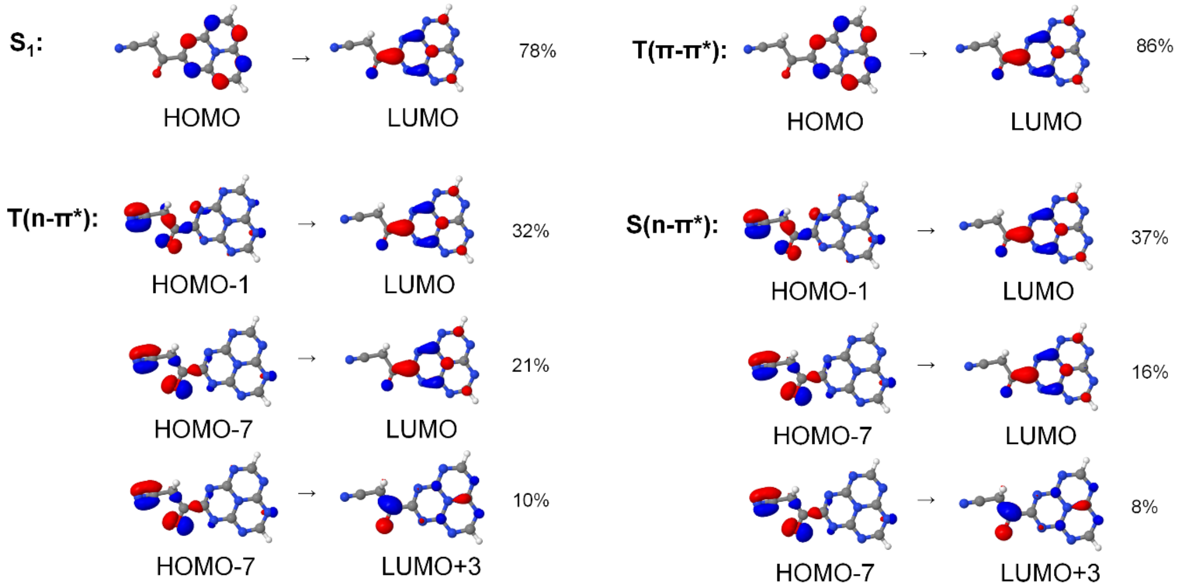

Figure S3. Dominant transitions of Molecule **3** for S_1, T(π-π*), and T(n-π*) state at S_0 geometry

4

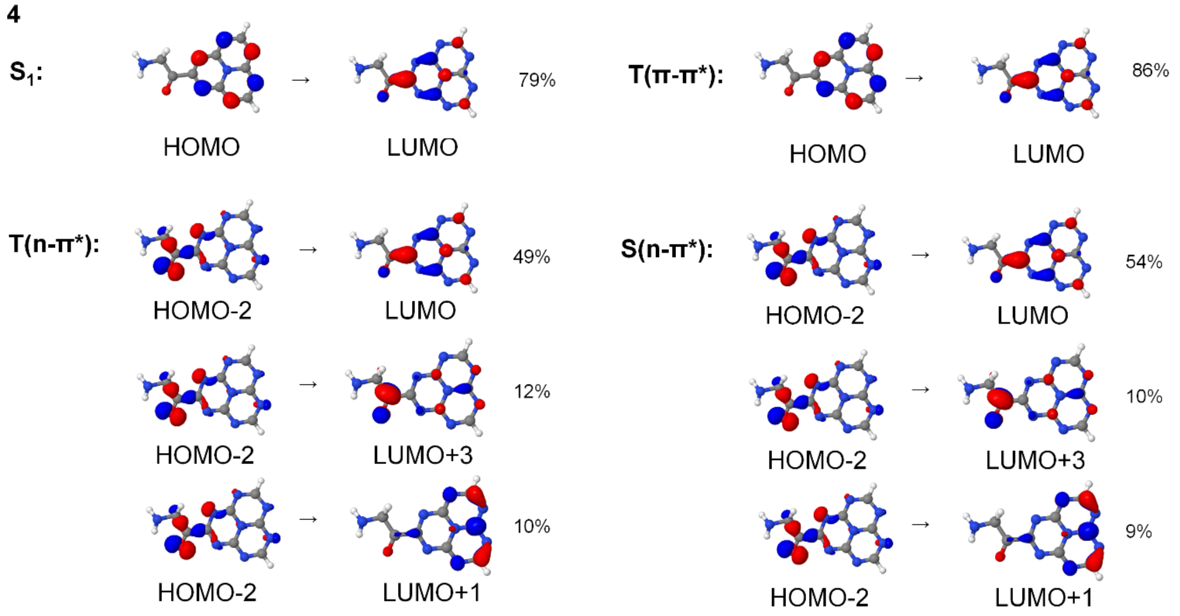

Figure S4. Dominant transitions of Molecule **4** for S_1, T(π-π*), and T(n-π*) state at S_0 geometry

Table S9. Computed S(n-π*) energy at geometry optimized using EOM-CCSD

Molecule	S(n-π*) Energy
2	3.087
3	3.215
4	2.618

Oscillator Strength

Table S10. Oscillator strength at S_1 geometries of each molecule

	Oscillator Strength
1	0.000
2	2.245×10^{-3}
3	3.927×10^{-3}
4	1.877×10^{-3}

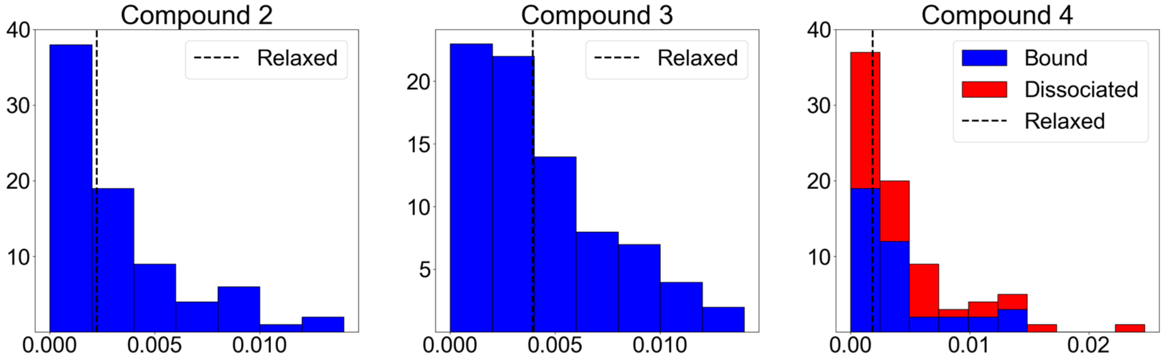

Figure S5. Histogram of oscillator strengths of molecules **2**~**4** at geometries sampled via Wigner Sampling, including the relaxed geometry. The oscillator strength at the relaxed geometry is marked with a dotted line. The sampled geometries of **4** include dissociated structure, the oscillator strength of which are indicated with red bars.

Dihedral angle of Heptazine Plane and Carbonyl Group

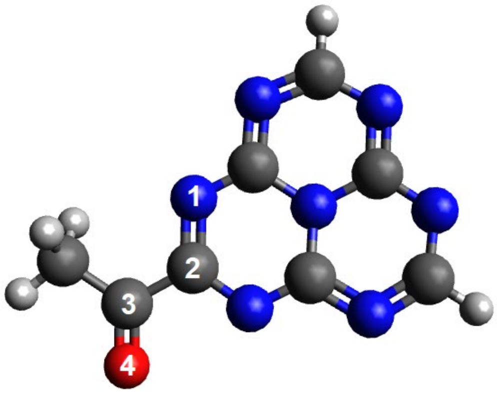

Figure S6. The dihedral angle of the planes made by 1-2-3 and 2-3-4 is measured

Table S11. Dihedral angles measured at the relaxed geometries of S_1 and T(π-π*) state of molecules **2~4**

	S_1	T(π-π*)
2	174.72	180.00
3	179.96	176.12
4	178.10	179.99

SOC at Wigner sampled geometries

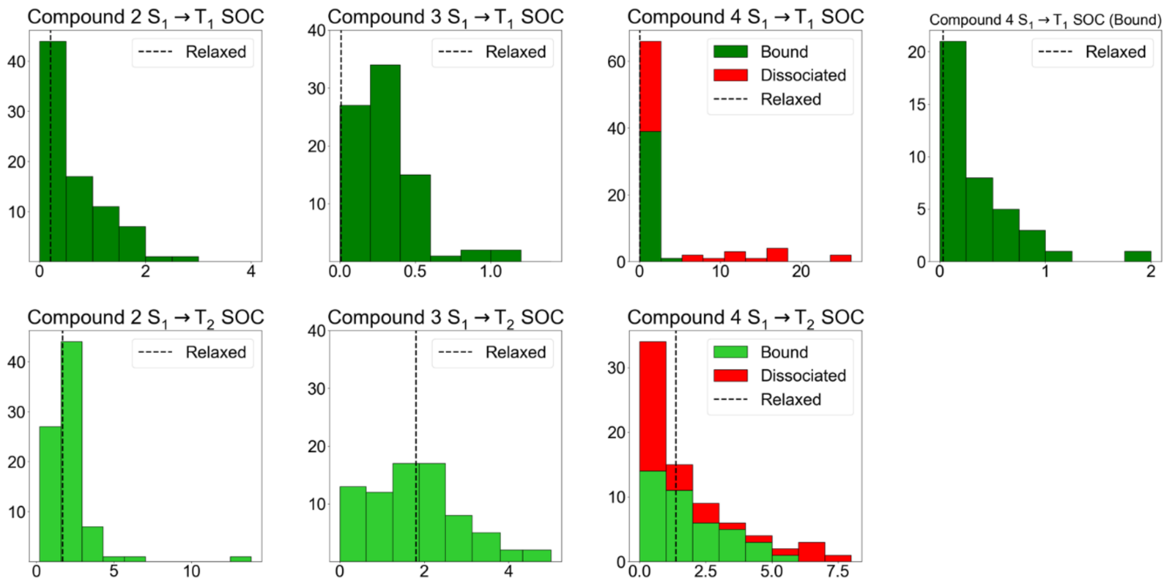

Figure S7. Histogram of spin orbit couplings (in cm^{-1}) of molecules **2**~**4** at geometries sampled via Wigner Sampling of the S$_1$ geometry, including the relaxed geometry. The spin orbit coupling at the relaxed geometry is marked with a dotted line. The sampled geometries of **4** include dissociated structure, the spin orbit coupling of which are indicated with red bars. As the dissociated structures of **4** shows wide range of SOC for S$_1$→T$_1$ transition, the histogram only containing the SOC from bound geometries is also included. The triplet states are labelled as T$_1$ and T$_2$ instead of (π-π*) and (n-π*) as the character of the states may get ambiguous at certain geometries.

Plot of Integrand for rISC

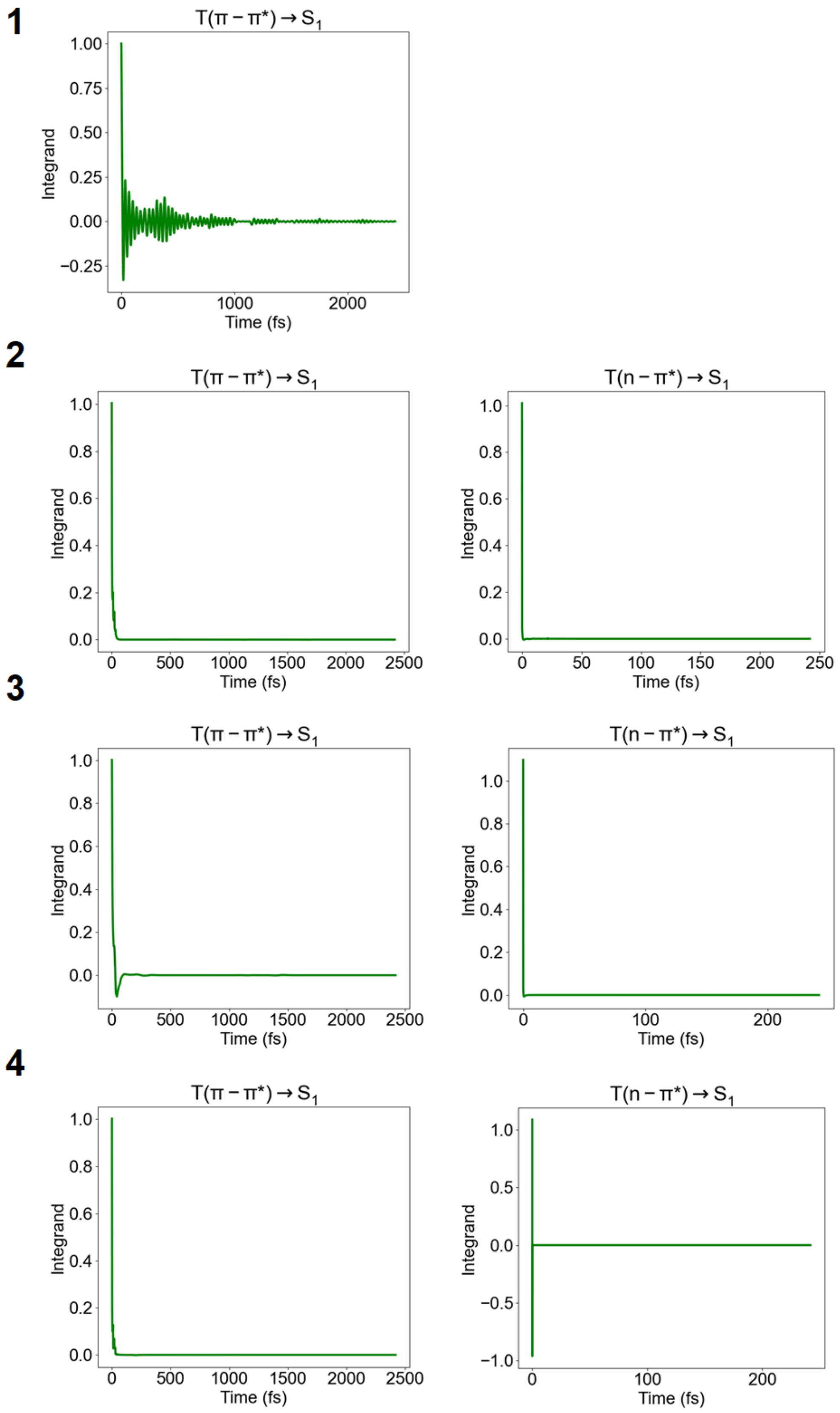

Figure S8. Plots of Integrand of for the rISC transitions of each molecule

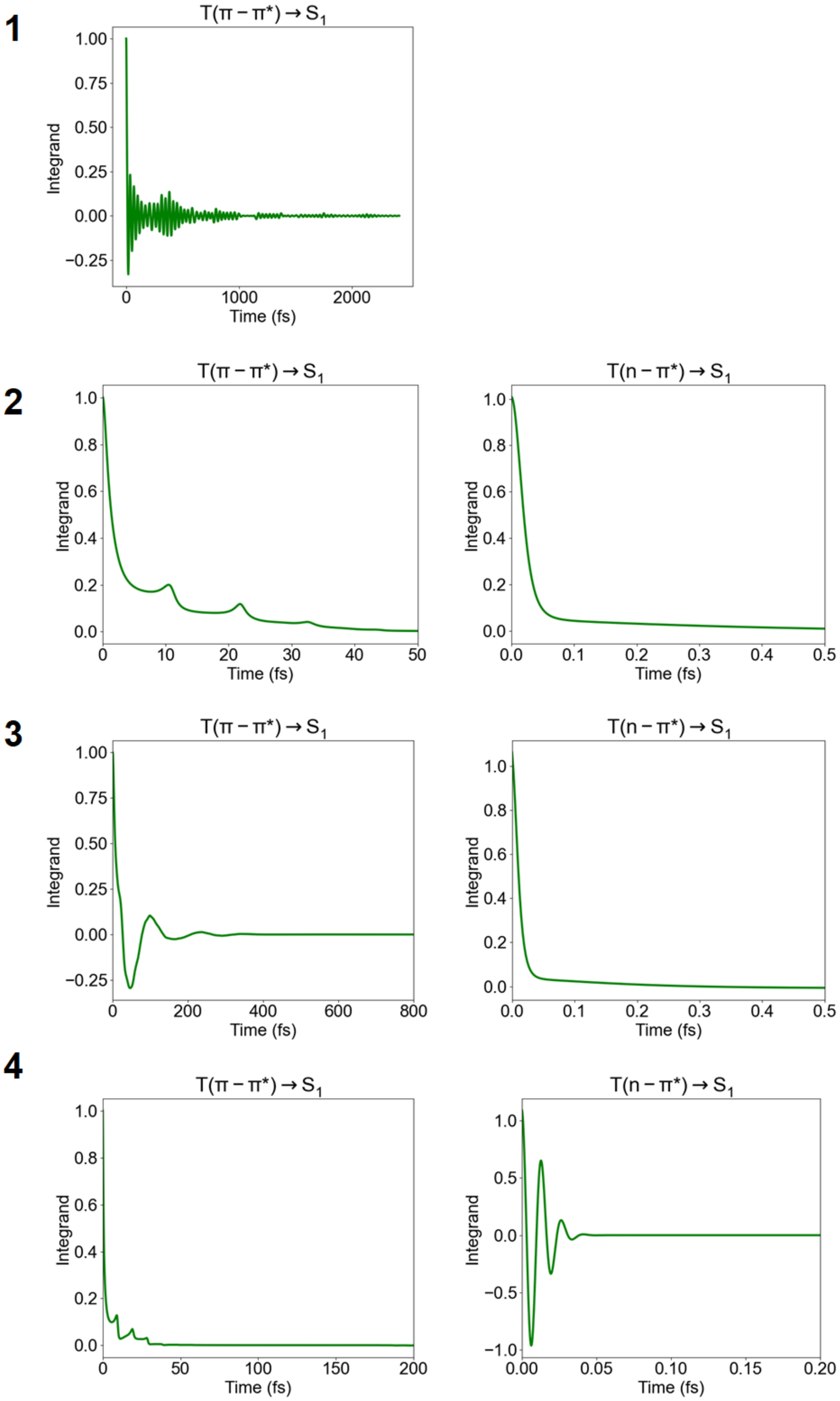

Figure S9. Plots of Integrand of for the rISC transitions of each molecule, with timescale adjusted for each plot for better visibility

Plot of Trace for IC

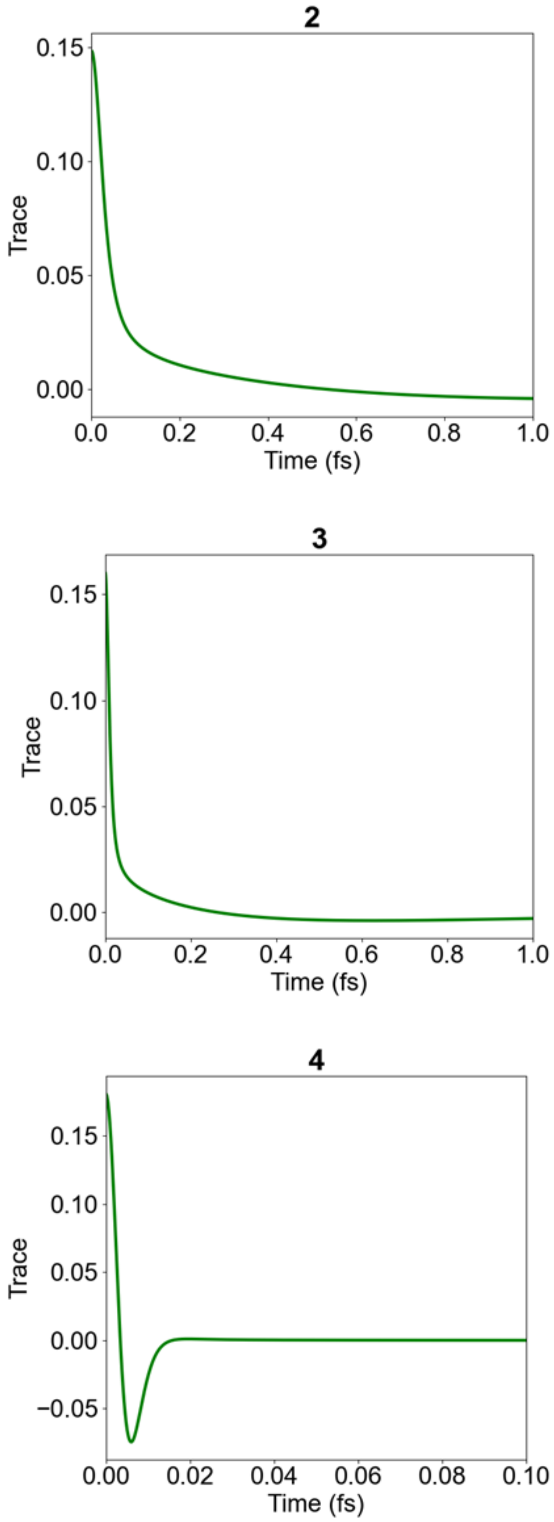

Figure S10. Plots of traces of $\rho_{kl}(\beta, \tau)$ in Equation (13) for molecules **2~4**

Normal modes with the largest displacement vectors

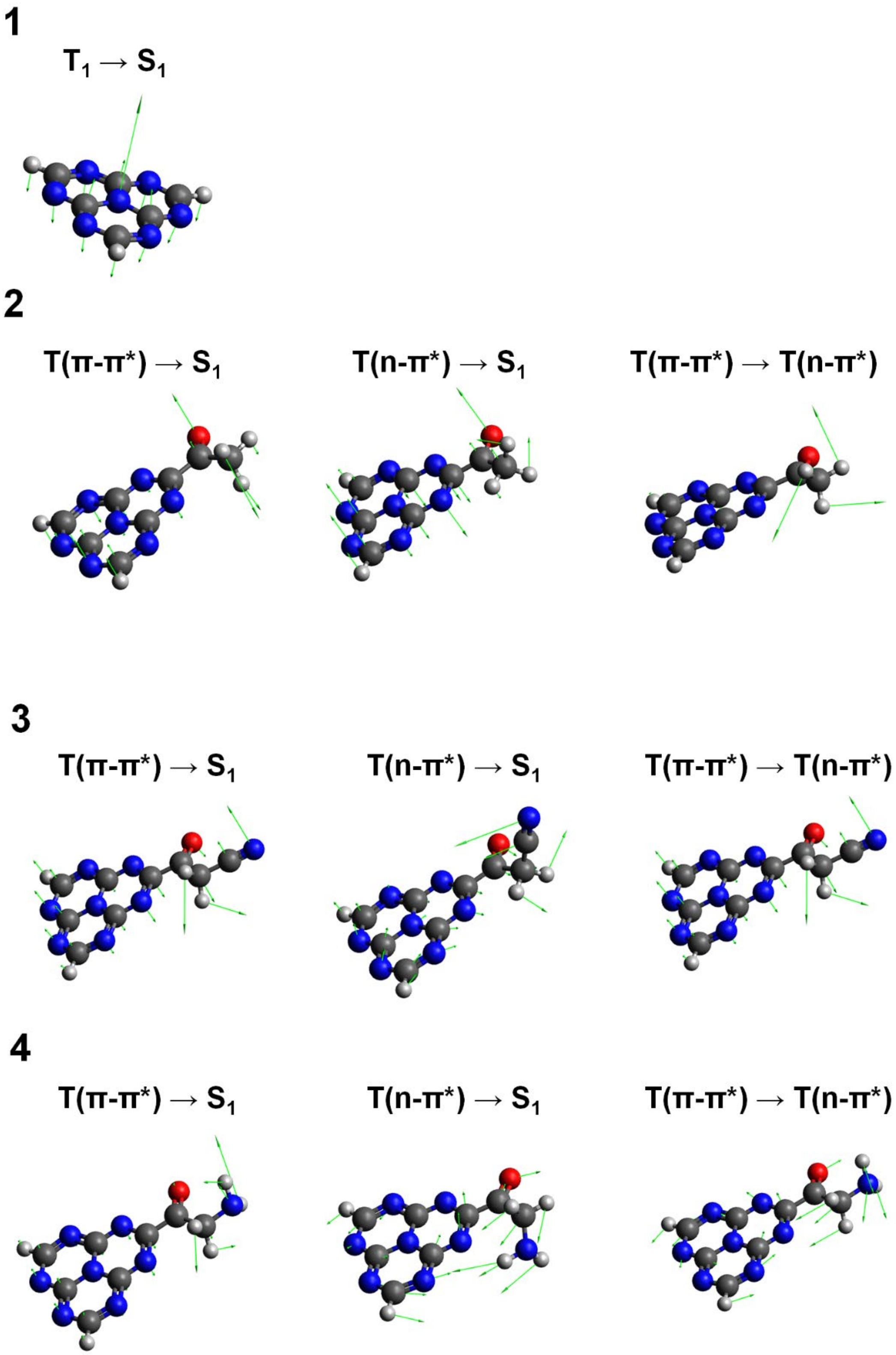

Figure S11. Plots of normal modes of the initial states with the largest displacement vector each transition

Rotation angles of the Duschinsky Matrix

The eigenvalues of the Duschinsky matrix were obtained to provide quantitative measures for the rotation of the normal modes upon the transitions of interest. The eigenvalues of a rotation matrix comprise a set of complex numbers with absolute value of 1, with the phase of each eigenvalue $e^{i\theta}$ signifying rotation by angle θ. θ of π/4 represents a rotation that mixes two vectors by 1:1 proportion, thus implying that the transition mixes the normal modes to a higher degree. We provide the angles of rotation of the Duschinsky matrices by taking the arcsin values of the imaginary parts of the eigenvalues.

Duschinsky Matrix and Displacement Vectors for IC

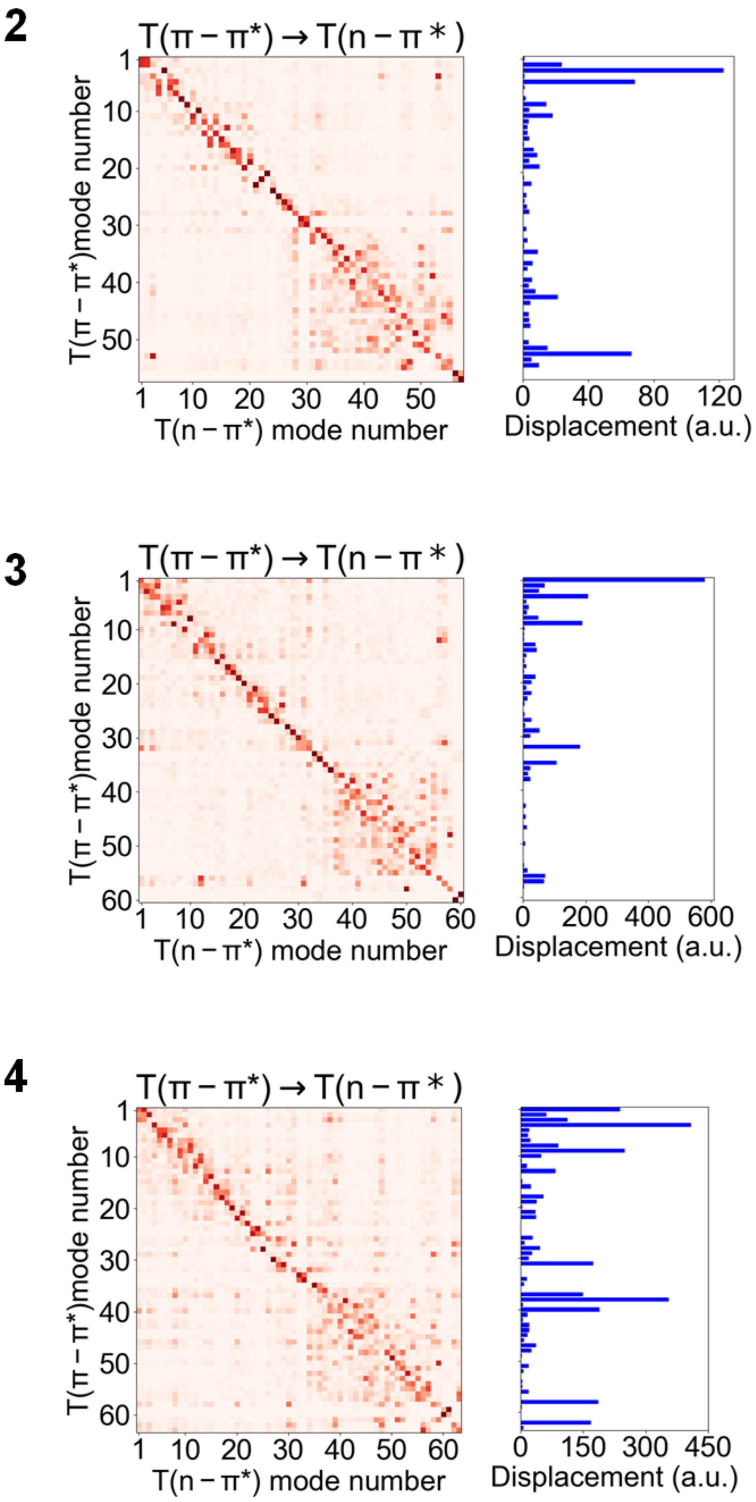

Figure S12. Plots of Duschinsky matrix and displacement vector for IC transitions of molecules **2** ~ **4**

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